RESERVE PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Dibenzoate Esters of Aliphatic Diols and process for their preparation

Union Careide CORPORATION, (formerly known as Union Carbide and Carbon Corporation), of 30, East 42nd Street, New York, State of New York, United States of America, a corporation organised under the laws of the State of New York, United States of America, (assignee of Gordon Murray Goodale, Edward James Mills, Jr., Thomas Robert Miller and James John 10 FASNACHT), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
This invention relates to a method of pre-

paring dibenzoate esters of aliphatic diols by reacting butyl benzoate with an aliphatic diol containing four to nine carbon atoms and having no tertiary hydroxyl groups. A tertiary 20 hydroxyl group is one which is attached to a

tertiary carbon atom. Among the compounds which may be pre-pared in accordance with the present invention are the dibenzoate esters of aliphatic diols having an oxygen interrupted carbon chain, such as diethylene glycol dibenzoate, dipropy-lene glycol dibenzoate, and polyalkylene glycol dibenzoates and the dibenzoate esters of straight and branched chain aliphatic diols having an uninterrupted carbon chain, such as having an uninterrupted carbon chain, such as 2-ethyl-1,3-heranediol; 2-methoxynethyl-2,4-dimethyl-1,5-pentanediol; 2,5-heranediol; 3-methyl-1,5-pentanediol; 2-ethyl-2-propalli; 2-methyl-1,3-propanediol; 2-diethyl-1,3-propanediol; 2-ethyl-1,5-pentanediol; 2-ethyl-1,5-pentanediol; 2-ethyl-1,5-pentanediol; 2-ethyl-1,5-pentanediol and 1,5-pentanediol.

Dibenzoate esters of aliphatic diols of the class described above are useful as vlasticines.

class described above are useful as plasticizers for vinyl resins. Dipropylene glycol dibenzoate is particularly valuable as a plasticizer for poly-

to 9 carbon atoms and which containing no tertiary hydroxyl group can be prepared by reacting one molecular proportion of one of the above described aliphatic diols with 2.5 molecular proportions of butyl benzoate in the presence of an alkaline catalyst. The reaction can be conducted at a temperature of from 100° C. to 250° C, and preferably from 150° C to 180° C, for a period of from 10 hours to 30 hours. Although the reaction can be conducted at a pressure of from 0.1 mm. Hg to 200 mm. Hg, it is preferably conducted at a pressure of from 2 mm. Hg to 100 mm. Hg. Suinable catalysts for the reaction comprise alkali metal and alkaline earth metal oxides, hydroxides, alkoxides, carbonates and borates. Preferred catalysts are the alkaline earth metal Preferred catalysts are the alkaline earth metal oxides. Calcium oxide is a particularly suitable catalyst because of irs good catalytic activity, low cost and ease of handling. Catalyst concentrations can vary from 0.06 per cent by weight to 1.4 per cent by weight but are preferably between 0.1 per cent by weight and 1.0 per cent by weight. By operating at a temperature in the range of from 158° C. to 180° C. with a catalyst concentration of 0.1 per cent by weight, excellent results are obtained, parby weight, excellent results are obtained, particularly in the production of dipropylene glycol dibenzoste. As the reaction proceeds, buttoned is removed by distillation, followed by a mid-fraction, usually containing butanol and butyl benzoate and a third fraction of butyl benzoate. The pure dibenzoate ester of the aliphatic diol can be isolated from the residue by distillation or by filtration. The following examples are illustrative:

EXAMPLE I.

Into a three-neck kettle equipped with thermowell, a mechanical stirrer and a 25 × 250 mm. column packed with glass Raschig rings and surmounted by a standard reflux head with vinyl chloride resins.

We have discovered that the dibenzoate essets of aliphatic diols which contain from 4 the usual condenser and vacuum receiver attached, were charged 8015 grams (45.0 mols) of refined buryl benzoate and 2414 grams (18.0

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mols) of dipropylene glycol. Then 104 grams (1.0 per cent by weight of the kettle charge) of calcium oxide were added and the reaction mixture was heated and stirred at a pressure of 100 mm. Hg. Butanol was removed by distillation at this pressure until the kettle temperature increased to 180-194° C. The kettle temperature was then reduced slightly, the pressure was reduced to 50 mm. Hg, and the remaining butanol was collected as distillate. A mid-fraction, containing butanol and butyl benzoate was then distilled, followed by a pure fraction of butyl benzoate. Occasional reductions in pressure were required to facilitate maintenance of the kettle temperature below 198° C. The contents of the reaction kettle were cooled, mixed with a filter aid and filtered to remove the catalyst. The filtrate was then charged to a stripping still equipped with a goose-neck head and an external nitrogen chullator. The stripping operation was conducted at a temperature of 182° C. at less than 1.0 mm. Hg. The kettle residue was then 1.0 mm. Hg. The kettle residue was then treated with a decolorizing material, filtered, and recovered.

A yield of 81.7 per cent of dipropylene glycol dibenzoate (based on dipropylene glycol) was obtained, with an efficiency (based on buyl benzoate) of 86.4 per cent. The refined dipropylene glycol dibenzoate had a purity by saponification of 99.8 per cent, an acidity (as benzoic acid) of 0.02 per cent, a diol content of 0.69 per cent and the following physical properties:-

Refractive index at 20° C. -Specific gravity (20/20° C.) 1.1255 Color (based on Pr-Co scale) 35

EXAMPLE IL

Into a three-neck kettle equipped with a thermowell, a mechanical stirrer and a 25 × 250 mm, column packed with glass Raschig rings and surmounted by a standard reflux head with the usual condenser and vacuum receiver attached, were charged 8015 grams (45.0 mols) of refined buryl benzozte and 2414 grams (18.0 mols) of dipropylene giycol. Then 104 grams (1.0 per cent by weight of the kettle charge) of calcium oxide were added and the reaction mixture was heated and stirred at a pressure of 100 mm. Hg. Butanol was removed by distillation at this pressure until the kettle temperature increased to 175—187° C. The kettle temperature was then reduced slightly, the pressure was reduced to 80 mm. Hg, and the remaining butanol was collected as distillate.

A mid-fraction, containing butanol and butyl benzoate was then distilled, followed by a pure fraction of butyl benzoate. Occasional reduc-

> Refractive index at 20° C. Specific gravity (20/20° C.) -Color (based on Gardner scale) Boiling range

tions in pressure were required to facilitate maintenance of the kettle temperature below C. The contents of the reaction kettle were cooled, mixed with a filter aid, and filtered to remove the catalyst. The filtrate was then charged to a stripping still equipped with a gooseneck head and an external nitrogen ebuliator. The stripping operation was carried out at a temperature of 210° C. and a pressure of 1.5 mm. Hg. The kettle residue was then treated with magnesol, filtered and recovered.

A yield of 82.6 per cent of dipropylene glycol dibenzoate (based on dipropylene glycol) was obtained, with an efficiency (based on butyl benzoate) of 87.3 per cent. The refined dipropylene glycol dibenzoate had a purity by saponification of 99.9 per cent, an acidity (as benzoic acid) of 0.06 per cent, a diol content of 0.72 per cent and a color (based on Pt-Co scale) of 35.

EXAMPLE III.

Into a three-neck kettle equipped with a thermowell, a mechanical stirrer and a 25×250 mm, column packed with glass Raschig rings and surmounted by a standard reflux head with the usual condenser and vacuum receiver attached, were charged 3565 grams (20.0 mols) of refined butyl benzoate and 1073 grams (8.0 mals) of dipropylene glycal. Then 23 grams (0.5 per cent by weight of the kettle charge) of calcium oxide were added and the reaction mixture was heated and stirred at a pressure of 100 mm. Hg. Butanol was removed by distillation at this pressure until the kettle temperature increased to 175-180° C. The kettle temperature was then reduced slightly, the pressure was reduced to 50 mm. Hg, and the 95 remaining butanol was collected as distillate. A mid-fraction, containing butanol and butyl benzoate was then distilled, followed by a pure fraction of butyl benzoate, Occasional reductions in pressure were required to facilitate 100 maintenance of the kettle remperature below 180° C. After most of the excess butyl benzoate had been collected, the pressure was reduced to 0.5 mm. Hg and the temperature of the kettle was raised as rapidly as possible to 105 around 205-207° C. The desired dipropylene glycol dibenzoate was then collected as stillate

A yield of 86.1 per cent of dipropylene glycol dibenzoste (based on dipropylene glycol) was obtained, with an efficiency (based on butyl benzoate) of 78.8 per cent. The refined dipropylene glycol dibenzoate had a punity (by saponification) of 99.9 per cent, an activity (as benzoate acid) of 0.05 per cent, a diel content of benzoic acid) of 0.05 per cent, a diol content of 115 0.22 per cent and the following physical properties:-

1.5297 1.1236

190-195° C. at 0.5 mm. Hg.

120

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EXAMPLE IV.

Into a three-neck kettle equipped with a thermowell, a mechanical stirrer and a 25 × 250 mm. column packed with glass Raschig rings and surmounted by a standard reflux head with the usual condenser and vacuum receiver attached, were charged 3565 grams (20.0 mols) of refined butyl benzoate and 1073 grams (8.0 mols) of dipropylene glycol. Then 4 grams (0.1 per cent by weight of the kettle charge) of calcium oxide were added and the reaction mixture was beated and stirred at a pressure of 100 mm. Hg. Butanol was removed by distillation at this pressure until the kettle temperature increased to 175—180° C. The kettle temperature was then reduced slightly, the pressure was reduced to 50 mm. Hg, and the remaining butanol was collected as distillate. A mid-fraction, comaining butanol and butyl

> Refractive index at 20° C. Specific gravity (20/20° C.) - Color (based on Pt-Co scale) -Boiling range

EXAMPLE V.

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85

Into a three-neck kettle equipped with a 45 thermowell, a mechanical stirrer and a 25 × 250 mm column packed with glass Raschig rings and surmounted by a standard refure head with the usual condenser and vacuum receiver attached, were charged 1782 grams (4.0 mols) of refined butyl benzoate and 537 grams (10.0 mols) of dipropylene glycol. Then 1.26 grams (0.06 per cent by weight of the kettle charge) of calcium oxide were added and the reaction mixture was heated and stirred at a pressure of 100 mm. Hg. Butanol was removed by distillation at this pressure until the heatite temperature increased to 175—180° C. The lettle temperature was then reduced slightly, the pressure was reduced to 50 mm. Hg., and the remaining butanol was collected as distillate. A mid-fraction, containing butanol and butyl benzante was then distilled; followed by a pure fraction of butyl benzoate. Occasional

> Refractive index at 20° C. Specific gravity (20/20° C.) - Color (based on Pt-Co scale) -Boiling range

Example VI

Into a three-next kentle equipped with a thermowell, a mechanical stirrer and a 25 × 250 mm. column packed with glass Raschig rings and surmounted by a standard reflux head with the usual condenser and vacuum receiver strached, were charged 2228 grams (12.5 mols) of refined buryl benzoate and 531 grams (5.0 mols) of diethylene glycol. Then 2.76 grams (0.1 per cent by weight of the kettle charge) of calcium oxide were added and the reaction mixture was heated and stirred at a pressure of 100 mm. Hg. Butanol was removed by distillation at this pressure until the kettle temperature increased to 175° C.

benzoate was then distilled, followed by a pure fraction of butyl benzoate. Occasional reductions in pressure were required to facilitate maintenance of the kettle temperature around 180° C. After most of the excess butyl benzoate had been collected, the pressure was reduced to 2.0 mm. Hg, and the temperature of the kettle was raised as rapidly as possible to around 215—220° C. The desired ester was then collected as distillate.

A yield of 81.2 per cent of dipropylene 30 glycol dibenzoate (based on dipropylene glycol discussare (used on impreyment glycol) was obtained, with an efficiency (based on buryl benzoare) of 90.2 per cent. The refined dipropylene glycol discussare had a purity (by saponification) of 99.9 per cent, an acidity (as benzoic acid) of 0.17 per cent, a diol content of 0.19 per cent and the following

physical properties:

1.5287 1.1224

210-216° C. at 2 mm. Hg.

reductions in pressure were required to facilitate maintenance of the kettle temperature below 180° C. The contents of the reaction kettle were cooled to 130° C, mixed with a filter aid, and filtered to remove the catalyst. The filtrate was then charged to a stripping still equipped with a gooseneck head and an 70 external nitrogen ebullator. The distillation of dipropylene glycol dibenzone was carried out at a kettle temperature of 212° C. and a pressure above 1.0 mm. Hg.

A yield of 58.1 per cent of dipropylene gly-col dibenzoate (based on dipropylene glycol) was obsuined, with an efficiency (based on buryl benzoate) of 74.0 per cent. The refined dipropolence glycol dibenzoate had a purity (by saponification) of 98.5 per cent, an acidity (as benzoic acid) of 0.03 per cent, a diol content of 1.50 per cent and the following physical

properties:-

1.1230

204° C. at 1 mm. Hg.

The kettle temperature was then reduced slightly, the pressure was reduced to 50 mm.
Hg., and the remaining butanol was collected 105 as distillate. A mid-fraction, containing butanol and butyl beazoate was then distilled, followed by a pure fraction of buryl benzoate. Occasional reductions in pressure were required to facilitate maintenance of the kettle temperature below 180° C. The contents of the reaction kettle were cooled to 130° C. mixed with a filter aid and filtered to remove the caralyst. The filtrate was then charged to a stripping still equipped with a gooseneck head and an external nitrogen ebullator. distillation of diethylene glycol dibenzoate was

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carried out at a temperature of 210-220° C. and a pressure above 1.0 mm. Hg.

A yield of 73.7 per cent of diethylene glycol dibenzoate (based on diethylene glycol) was obtained, with an efficiency (based on buryl benzoate) of 762, per sent. The refined benzoate) of 76.2 per cent. The refined

> Refractive index at 20° C. Specific gravity (20/20° C.) - Color (based on Pt-Co scale) -Boiling range -

EXAMPLE VII

Into a three-neck kettle equipped with a thermowell, a mechanical stirrer and a 25 × 250 mm. column packed with glass Raschig rings and surmounted by a standard reflex head with the usual condenser and vacuum receiver attached, were charged 2230 grams (12.5 mols) of refined butyl benzoate and 731 grams (5.0 mols) of 2-ethyl-1,3-hexanediol. grams (1.0 per cent by weight of the kettle charge) of calcium oxide were added and the reaction mixture was heated and stirred at a pressure of 100 mm. Hg. Butanol was removed by distillation at this pressure until the kettle temperature increased to 198° C. The kettle temperature was then reduced slightly, the pressure was reduced to 50 mm. Hg. and the remaining butanol was collected as distillate. A mid-fraction, containing butanol and butyl benzoate was then distilled, followed by a pure fraction of butyl benzoate. Occasional reductions in pressure were required to facilitate maintenance of the kettle temperature around 200° C. After most of the excess butyl benzoate had been collected a stripping operation was carried out for ren minutes at a temperature of 220° C. and a pressure of 1.5 mm. Hg. The kettle residue pressure of 1.5 mm. Hg. The was then filtered and recovered.

A yield of 88.4 per cent of 2-ethyl-1,3-hexanedial dibenzante (based on 2-ethyl-1,3heranediol) was obtained, with an efficiency (based on butyl benzoare) of 84.0 per cent. The refined 2-ethyl-1,3-hexanodiol dibenzoate had a purity (by saponification) of 99.4 per cent, an acidity (as benzoic acid) of 0.14 per cent, a dici content of 0.2 per cent and the following physical properties:— Specific gravity (20/20° C.)— Color (based on Gardner scale)—

EXAMPLE VIII

Into a three-neck kettle equipped with a thermowell, a mechanical stirrer and a 25 × 250 mm. column packed with glass Raschig rings and surmounted by a standard reflux head with the usual condenser and vacuum receiver attached, were charged 2230 grams (12.5 mols) of refined buryl benzoate and 731 grams (5.0 mols) of 2-ethyl-1,3-hexanediol. Then 30 grams (LO per cent by weight of the kettle charge) of calcium oxide were added and the reaction mixture was heated and stirred at a diethylene glycol dibenzoate had a purity (by saponification) of 98.9 per cent, an acidity (as benzoic acid) of 0.07 per cent, a diel content of 1.0 per cent and the following physical pro- 10

1.5438 1.1746 80

200-214° C. at 1 mm. Hg.

ressure of 100 mm. Hg. Butanol was removed by distillation at this pressure until the kettle temperature increased to 196° C. The kettle temperature was then reduced slightly, the pressure was reduced to 50 mm. Hg., and the remaining butanol was collected as distillate. A mid-fraction, containing butanol and butyl benzoate was then distilled, followed by a pure fraction of butyl benzoate. Occasional reductions in pressure were required to facilitate maintenance of the kettle temperature below 200° C. The contents of the reaction kettle were cooled to around 130° C, mixed with a filter aid and filtered to remove the catalyst. The filtrate was then charged to a stripping still equipped with a gooseneck head and an external nitrogen ebullator. The stripping external nirrogen ebullator. The stripping operation was carried out at 192° C. and 1 mm. Hg. The kettle residue was then filtered and recovered.

A yield of 75.0 per cent of 2-ethyl-1,3hexanediol dibenzoate (based on 2-ethyl-1,3hexanediol) was obtained, with an efficiency (based on butyl benzoate) of 77.5 per cent. The refined 2-ethyl-1,3-hexanediol dibenzoate had a purity (by saponification) of 99.0 per cent, an acidity (as benzoic acid) of 0.18 per cent, a diol content of 0.52 per cent and the following 95

physical properties:—
Refractive index at 20° C.
Specific gravity (20/20° C.) 1.5317 1.0814 Color (based on Gardner scale)

EXAMPLE IX

Into a three-neck kettle equipped with a thermowell, a mechanical stirrer and a 25 × 250 mm. column packed with glass Raschig rings and surmounted by a standard reflux head with the usual condenser and vacuum receiver 105 attached, were charged 1068 grams (5.99 mols) of refined buryl benzoate and 441 grams (2.5 mols) of 2-methoxymethyl-2,4-dimethyl-1,5-pentanediol. Then 15 grams (1.0 per cent by weight of the kettle charge) of calcium oxide were added and the reaction mixture was heated and stirred at a pressure of 100 mm. Hg. Butanol was removed by distillation at this pressure until the kettle temperature increased to 175-180° C. The kettle temperature was 115 then reduced slightly, the pressure was reduced to 50 mm. Hg., and the remaining butanol was collected as distillate. A mid-fraction, containing butanol and buryl benzoate was then

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distilled, followed by a pure fraction of butyl benzoate. Occasional reductions in pressure were required to facilitate maintenance of the kettle temperature below 180° C. The contents of the reaction kettle were cooled to 130° C., mixed with a filter aid and filtered to remove the catalyst. The filtrate was then charged to a stripping still equipped with a gooseneck head and an external ninogen chullator. Distillation of 2-methoxymethyl-2,4-dimethyl-1,5-pentanediol dibenzoate was extred out at a temperature of 232° C. and a pressure of 1.5 mm. Hg.

A yield of 83.1 per cent of 2-methoxymethyl-2,4-dimethyl-1,5-pentanediol dibenzoate (based 2 - methoxymethyl-2,4-dimethyl-1,5-penmnediol) was obtained, with an efficiency (based on buryl benzoate) of 79.0 per cent. The refined 2-methoxymethyl-2,4-dimethyl-1,5pentanedial dibenzate had a purity (by saponification) of 99.8 per cent an acidity (as benzoic acid) of 0.14 per cent, essentially no dial content and the following physical properties:-

Refractive index at 20° C.

25

30

70

Specific gravity (20/20° C.) - Color (based on Pr-Co scale) -Boiling point

EXAMPLE X

Into a three-neck kettle equipped with a thermowell, a mechanical stirrer and a 25 × 250 mm. column packed with glass Reschig rings and surmounted by a standard reflux head with the usual condenser and vacuum receiver attached, were charged 446 grams (2.5 mols) of refined butyl beazoste and 160 grams (1.0 mols) of 2,4-diethyl-1,5-pentanediol. Then 5 grams of calcium oxide were added and the reaction mixture was beated and stirred at a pressure of 100 mm. Hg. Butanol was comoved by distillation at this pressure until the kettle temperature increased to 175—189° C. The kettle temperature was then reduced slightly, the pressure was reduced to 50 mm. singiny, the pressure was remark to 30 mm. Hg., and the remaining butanol was collected as distillate. A mid-fraction, containing butanol and butyl benzoare was then distilled, followed by a pure fraction of butyl benzoare.

Refractive index at 20° C. Specific gravity (20/20° C.) Color (based on Pr-Co scale) Boiling point -

EXAMPLE XI

Into a three-neck kettle equipped with a 75 thermowell, a mechanical stirrer and a 25 × 250 mm. column packed with glass Raschig rings and surmounted by a standard reflux head with the usual condenser and vacuum receiver attached, were charged 8015 grams (45 mols) of refined butyl benzoate and 2125 grams (18 mols) of 3-methyl-1,5-pentanediol. Then 101 grams (1.0 per cent by weight of the kettle charge) of calcium oxide were added and the reaction mixture was heated and stirred at a pressure of 100 mm. Hg. Butanol was removed by distillation at this pressure until the kettle temperature increased to 190-200° C. The kettle temperature was then reduced slightly, the pressure was reduced to 50 mm. Hg., and the remaining butanol was collected as distillate. A mid-fraction, containing butas distillate. A mid-traction, containing our-anol and buryl benroate was then distilled, followed by a pure araction of butyl benzoate,

225° C, at 1.5 mm. Hg. Occasional reductions in pressure required to facilitate maintenance of the kettle temperature below 180° C. The contents of

1.5310

1.1003

the reaction kettle were cooled to 130° C., mixed with a filter aid and filtered to remove the catalyst. The filtrate was then charged to a stripping still equipped with a gnoseneck head and an external nitrogen ebullator. Distiliation of 2,4-dicthyl-1,5-pentanediol dibenzoate was carried out at a temperature of 254 C. and a pressure of 4.0 mm. Hg.
A yield of 36.9 per cent of 2,4-diethyl-1,5-

pentanedial dibenzoate (based on 2,4-diethyl-1,5-pentanedial) was obtained, with an efficiency (based on butyl benzoate) of 44.8 per cent. The refined 2,4-diethyl-1,5-pentanediol dibenzone had a purity (by saponification) of 99.6 per cent, an acidity (as benzole acid) of 0.62 per cent, a diol coment of 0.04 per cent and the following physical properties:—

1.5322 1.0775

30 206° C. at 1 mm, Hg.

Occasional reductions in pressure required to facilitate maintenance of the kettle temperature below 190° C. The contents of the reaction kettle were cooled, mixed with a filter aid and filtered to remove the catalyst. The fibrate was then charged to a stripping still equipped with a governeck head and an external nitrogen ebullator. The stripping operation was carried out at a kettle temperature of 180—189° C. and a pressure of 2 to 4 mm. He. The kettle residue was then filtered and

A yield of 85.3 per cent of 3-methyl-1,5pentanediol dibenzoate (based on 3-methyl-1,5pentamediol) was obtained, with an efficiency (based on buryl benzoare) of 86.6 per cent. The refined 3-methyl-1,5-pentamediol dibenzoate had a purity (by saponification) of 100.2 per cent, an acidity (as benzoic acid) of 0.01 per cent, essentially no dial content and the following physical properties:-

50

95

815.991 Refractive index at 20° C. 1.5378 Specific gravity (20/20° C.) -Color (based on Pt-Co scale) -1.1103 186 -192° C. at 1 mm. Hg. Boiling range -33.4° C. Freezing point EXAMPLE XII tions in pressure were required to facilitate Into a three-neck kettle equipped with a thermowell, a mechanical stirrer and a 25 × 250 maintenance of the kettle temperature below 160° C. The contents of the reaction kettle mm. column packed with stainless steel pro-truded packing and surmounted by a standard reflux head with the usual condenser and were cooled, mixed with a filter aid and filtered to remove the catalyst. The filtrate was then charged to a stripping still equipped with vacuum receiver attached, were charged 1338 grams (7.5 mols) of refined butyl benzoate and a gooseneck head and an external nitrogen ebullator. Distillation of 2-ethyl-2-butyl-1,3-propanediol dibenzoate was carried out at a temperature of 237—267° C, and a pressure 480 grams (3.0 mols) of 2-ethyl-2-butyl-1,3propanediol. Then 18.2 grams (1.0 per cent by weight of the kettle charge) of calcium of 1.5 mm. Hg.
A yield of 64.7 per cent of 2-ethyl-2-butyloxide were added and the reaction mixture 3-propanediol dibenzoate (based on 2-ethylwas heated and stirred at a pressure of 90 mm. Buranol was removed by distillation at 2-butyl-1,3-propanediol) was obtained, with an this pressure until the kettle temperature increased to 140° C. The kettle temperature efficiency (based on butyl benzoate) of 87.4 per cent. The refined 2-ethyl-2-buryl-1,3was then reduced slightly, the pressure was reduced to 75 mm. Hg., and the remaining butanol was collected as distillate. A midpropanediol dibenzoate had a purity (by saponi-fication) of 100.8 per cent, an acidity (as benzoic said) of 0.02 per cent, diol content of 0.39 per cent and the following physical profraction, containing butanol and butyl benzo-ate was then distilled, followed by a pure fracperties:tion of butyl benzoate. Occasional reduc-Refractive index at 20° C. 1.5327 Specific gravity (20/20° C.) - Color (based on Pt-Co scale) -1.0778 20 236° C. at 1.5 mm. Hg. Boiling range distilled, followed by a pure fraction of buryl benzoate. Occasional reductions in pressure EYAMPLE XIII Into a three-neck kettle equipped with a thermowell, a mechanical stirrer and a 25 × 250 were required to facilitate maintenance of the mm, column packed with stainless steel prokettle temperature below 170° C. The contruded packing and surmounted by a standard refinx head with the usual condenser and tents of the reaction kettle were cooled, mixed with a filter aid and filtered to remove the catavacuum receiver attached, were charged 200 The filtrate was then charged to a stripgrams (1.5 mole) of 2-methyl-2-propyl-1,3-proping still equipped with a gooseneck head and panediol and 670 grams (3.75 mois) of refined buryl benroate. Then 9 grams of calcium ordic (1.0 per cent by weight of the kettle an external nitrogen ebullator. Distillation of the ester was carried out at a kettle temper ture of 249-252° C. and a pressure of 2.0 charge) were added and the reaction mixture mm. Hg. A yield of 48.2 per cent of 2-methyl-2-pro-pyl-1,3-propanediol dibenzoate (based on 2was heated and stirred at a pressure of 100 mm. Hg. Butanol was removed by distillation at this pressure until the kettle tempera-ture rose to 156° C. The kettle temperature was reduced slightly, the pressure was reduced 70 to 50 mm. Hg., and the remaining butanol was collected as distillate. A mid-fraction, conmethyl - 2 - propyl - 1,3 - propanediol) was obtained. The refined 2-methyl-2-propyl-1,3propanediol dibenzoate had a purity of 101.8 (by saponification), essentially no acidity and 90 diol content and the following physical proper-A mid-fraction, containing butanol and butyl benzoate was then ties:--Refractive index at 20° C. 1 5367 Specific gravity (20/20° C) -1.1003 20 Color (based on Pt-Co scale) -

Boiling range -Freezing point -BYAMPLE XIV

In a three-neck kettle equipped with 100 thermowell, a mechanical stirrer and a 25 × 250 mm. column packed with stainless steel protruded saddles, and sucmounted by a standard reflux head with the usual condenser and vacuum receiver attached, were charged 670 grams (3.75 mols) of refined buryl benzoate and 105 200 grams (1.5 mols) of 2,2-diethyl-1,3-propanediol. Then 9 grams of calcium oxide (1.0 per cent by weight of the kettle charge) were added and the reaction mixture was

214° C. at 2 mm, Hg.

-5.6° C,

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heared and stirred at a pressure of 100 mm. charged to a stripping still equipped with a Butanol was removed by distillation at gooseneck head and an external nitrogen ebulpressure until the kettle temperature cased to 165° C. The kettle temperature lator. Distillation of the ester was carried increased to 165° C. out at a kettle temperature of 200° C, and a was then reduced slightly, the pressure was pressure of 2.0 mm. Hg. 20 reduced to 50 mm. Hg., and the remaining A yield of 42.9 per cent of 2,2-diethyl-1,3. butanol was collected as distillate. A midropanediol dibenzoste (based on 2,2-diethylfraction containing butanol and butyl benzo-ate was then distilled, followed by a pure frac-1,3-propandial) was obtained, with an efficiency (based on butyl benzoate) of 51.1 per tion of buryl benzoate. Occasional reduc-The refined 2,2-diethyl-1,3-propanediol dibenzoate had a purity of 101.2 per cent (by seponification), essentially no acidity, a diol content of 0.34 per cent, and the following tions in pressure were required to facilitate maintenance of the kettle temperature below The contents of the reaction kettle were cooled, mixed with a filter aid and filtered to remove the catalyst. The filtrate was then physical properties:-30 Refractive index at 20° C. 1.5402 Specific gravity (20/20° C.) - Color (based on Pt-Co scale) -1.1097 18 211—214° C. at 2 mm. Hg. —5° C. Boiling range -Freezing point -211-fraction of butyl benzoate, Occasional reduc-35 EXAMPLE XV Into a three-neck kettle equipped with a tions in pressure were required to facilitate maintenance of the kettle temperature below 195° C. The contents of the reactor kettle thermowell, a mechanical stirrer and a 25 x 250 mm. column packed with glass Raschig rings and surmounted by a standard reflux head with were cooled, mixed with a filter aid and filtered and surmounted by a standard reduce when the usual condenser and vacuum receiver attached, were charged 802 grams (4.5 mois) of refined buyl benzoate and 236 grams (2.0 to remove the catalyst. The filtrate was then charged to a stripping still equipped with a gooseneck head and an external mirrogen chul-lator. Distillation of the exter was carried mols) of 2-methyl-1,5-pentanediol. Then 10 grams of calcium oxide (1.0 per cent by weight of the kettle charge) were added and the reac-Distillation of the ester was carried out at a kettle temperature of 200 to 210° C. at 2.0 mm, Hg. A yield of 88.3 per cent of 2-methyl-1,5-pentanedial dibenzoate (based on 2-methyl-1,5tion mixture was heated and stirred at a pressure of 100 mm. Hg. Butanol was removed by distillation at this pressure until the kettle pentanedial) was obtained, with an efficiency of 88.8 (based on butyl benzoate). temperature increased to 171° C. The kettle The refined 2-methyl-1,5-pentanediol dibenzone had a purity of 99.8 per cent (by saponification) an acidity (as benzoic acid) of 0.12, essentially no diol content and the following physical protemperature was reduced slightly, the pressure was reduced to 50 mm. Hg., and the remaining butanol was collected as distillate, mid-fraction, containing butanol and butyl benzoate was then distilled, followed by a pure perties:-75 Refractive index at 20° C. 1.5379 Specific gravity (20/20° C.) 1.1045 Color (based on Pt-Co scale) -18 -204° C, at 2 mm. Hg. Boiling range -203-Freezing point --3.8° C. 80 EXAMPLE XVI butanol was collected as distillate. A mid Into a three-neck kentle equipped with a fraction, containing butanol and butyl benzo-ate was then distilled, followed by a pure fracthermowell, a mechanical stirrer and a 25 × 250 mm. column packed with stainless steel pro-truded packing and surmounted by a standard reflux head with the usual condenser and tion of butyl benzoate. Occasional reductions in pressure were required to facilitate maintenance of the kettle temperature below vacuum receiver attached, were charged 850 187° C The coments of the reaction kettle grams (4.77 mols) of refined butyl benzoate were cooled, mixed with a filter aid and filtered 105 to remove the canalyst. The filtrate was then and 264 grams (2.0 mols) of 2-ethyl-1,5-pen-tanedial. Then 11 grams of calcium oxide tanedial. Then 11 grams of calcium oxide (1.0 per cent by weight of the kettle charge) charged to a stripping still equipped with a gooseneck head and an external nitrogen ebulwere added and the reaction mixture was heated and stirred at a pressure of 100 mm. lator. Distillation of the ester was carried our at a kettle temperature of 218-221° C. 110 Butanol was removed by distillation at pressure until the kettle temperature ased to 154° C. The kettle temperature and a pressure of 1.5 mm. Hg.
A yield of 89.8 per cent of 2-ethyl-1,5-pen-

tanediol dibenzoste (based on 2-ethyl-1,5-pen-

tanedial) was obtained with an efficiency (based on butyl benzoate) of 91.4 per cent.

increased to 154° C.

was then reduced slightly, the pressure was reduced to 50 mm. Hg., and the remaining

refined 2-ethyl-1,5-pentanedial dibenzoate had a purity (by saponification) of 99.9 per cent, an acidity (as benzois acid) of 0.13 per cent, and a diol content of 0.69 per cent, and the following physical properties:-Refractive index at 20° C. 1.5356 Specific gravity (20/20° C.) - Color (based on Pt-Co scale) -1.0945 20 -218° C, at 1.5 mm. Hg. Boiling range 215--35° C. 10 Freezing point -Example XVII butyl benzoate. Occasional reductions in Into a three-neck kettle equipped with pressure was required to facilitate maintenthermowell, a mechanical stirrer and a 25 × 250 ance of the kettle temperature below 212° C mm. column packed with glass Raschig rings The contents of the reaction kettle were cooled, 15 and surmounted by a standard reflux head with mixed with a filter aid and filtered to remove the usual condenser and vacuum receiver the catalyst. The filtrate was then charged attached, were charged 620 grams (3.48 mols) of refined buryl benzoate and 200 grams (1.31 to a stripping still equipped with a gooseneck head and an external nitrogen ebullator. Dis-tillation of the ester was carried out at a kettle of 2-ethyl-3-methyl-1,5-pentanedial. mols) Then 8 grams (1.0 per cent by weight of the kettle charge) of lime (technical grade calcium oxide) were added and the reaction mixture temperature of 217-222° C. and a pressure of 2.0 mm, Hg.
A yield of 86.0 per cent of 2-ethyl-3-methyl1,5-pentanediol dibenzoste (based on 2-ethylwas heated to 110° C. and stirred at a pressure of 100 mm. Hg. Butanol was removed by distillation at this pressure until the kettle temperature increased to 190° C. The kettle 3-methyl-1,5-pentanedial) was obtained, with an efficiency (based on butyl benzoate) of 79.7 per cent. The refined 2-cthyl-3-methyl-1,5temperature was then reduced slightly, the pressure was reduced, and the remaining butpentanedial dibenzoase had a purity of 98.7 per cent (by sapanification), an acidity (as benzole acid) of 0.12 per cent, a dial content of 0.41 anol was collected as distillate. A mid-fraction, containing butanol and butyl benzoare was per cent and the following physical properthen distilled, followed by a pure fraction of Refractive index at 20° C. 1.5362 Specific gravity (20/20° C) -Color (based on Pt-Co scale) -1.0945 55 12 210--218° C. at 2 mm, Hg. Boiling range −17.2° C. Freezing point of from 2 mm. of mercury to 100 mm. of mer- 85 WHAT WE CLAIM IS:-1. Process for preparing dibenzoate esters 60 of aliphatic diols which comprises reacting 9. Process as claimed in any of Claims 1 to 8 butyl benzoate with an aliphatic diol containin which the aliphatic did is dipropylene giycol. ing 4 to 9 carbon atoms and having no tertiary hydroxyl groups as hereinhefore defined. 10. The dibenzoate ester of 2-ethyl-1,3- 90 2. Process as claimed in Claim 1 in which hexane diol. 65 one malecular proportion of the aliphatic dial is reacted with 2.5 molecular proportions of 11. The dibenzoste ester of 2-methyl-1:5pentanedici. 12. The dibenzoate ester of 2-ethyl-1,5butyl benzoate. 3. A process as claimed in Claim 1 or 2 in which the reaction is effected in the presence pentanediol. 13. The dibenzoste ester of 2-ethyl-3-70 of an alkaline catalyst. methyl-1,5-pentanediol. 4. Process as claimed in Claim 3 in which 14. The dibenzoate ester of 2,4-diethyl-1,5the alkaline catalyst is an alkali metal or alkapentanediol. • line earth metal oxide, hydroxide, alkoxide, car-15. The dibenzoare ester of 2-ethyl-2-butyl- 100 1,3-propanediol.

16. The dibenzoate ester of 2-methyl-2bonate or borate. 5. Process as claimed in Claim 4 in which propyl-1,3-propanediol.

17. Process for preparing dibenzoare esters of aliphatic diols substantially as herein desthe alkaline earth metal oxide is calcium oxide.
6. Process as claimed in Claim 3, 4 or 5 in which the catalyst concentration is between 0.1% and 1.0% by weight.
7. Process as claimed in any of Claims 1 to cribed with reference to and as illustrated in

> W. P. THOMPSON & CO., 12, Church Street, Liverpool, 1, Chartered Patent Agents.

the foregoing examples.

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6 in which the reaction is effected at a temperature of from 150° C. to 180° C.

8. Process as claimed in any of Claims 1 to

7 in which the reaction is effected at a pressure